

AMMOXIDATION OF 3-PICOLINE
ON UNPROMOTED AND ON TITANIUM-
AND TIN-PROMOTED VANADIUM
OXIDE CATALYSTS

ARNE ANDERSSON

DISSERTATION

1982

DEPARTMENT OF CHEMICAL TECHNOLOGY

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AND ON TITANIUM- AND TIN-PROMOTED
VANADIUM OXIDE CATALYSTS

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By due permission of the chancellor's office at Lund University for obtaining a doctorate, this thesis will be defended publicly in lecture-hall C at the Chemical Center, Lund, on May 13, 1982 at 10.15 a.m.

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Title and subtitle Ammonoxidation of 3-picoline on unpromoted and on titanium- and tin-promoted vanadium oxide catalysts.		
Abstract The ammonoxidation of 3-picoline to nicotinonitrile was studied over unpromoted and Ti- and Sn-promoted vanadium oxide catalysts. Activity studies of unpromoted catalysts revealed that the activity decreased in the order: $V_6O_{13} > V_2O_5 > V_2O_4$. X-Ray diffraction analysis was used to determine the phases present in the catalysts. The average oxidation number of vanadium was determined by a titrimetric method. It was found that catalysts with both V_2O_5 and V_6O_{13} phases present, were active and especially more selective than any of the pure oxides. Infrared investigations indicated that the role of SnO_2 was to weaken the V=O bonds. This can probably be seen as a consequence of the incorporation of Sn^{4+} in the V_2O_5 lattice. A band at 995 cm^{-1} was observed in the spectra of pre-reduced V-Ti-O catalysts. It is proposed that this band can be assigned to V=O bonds in a nonstoichiometric V_2O_5 or V_6O_{13} phase. The acidity and basicity of the pre-reduced V-Ti-O catalysts was determined by adsorption of NH_3 and CO_2. Activities and selectivities could be correlated. The charge distribution around the V-O bonds in pure vanadium oxides has been calculated by using an empirical formula. The same equation was used to calculate the oxygen bond strength on surfaces. The surfaces of lower oxides were treated as though they were in an oxidized state.		
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AND TIN-PROMOTED VANADIUM OXIDE CATALYSTS

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The thesis consists of this summary and the following papers,
referred to in the text by their Roman numerals:

- I. Activities of Vanadium Oxides in Ammoxidation
of 3-Picoline
A. Andersson and S.T. Lundin, J. Catal. 58, 383(1979) .
- II. Activities of V-Ti-O Catalysts in the Ammoxidation
of 3-Picoline
A. Andersson and S.T. Lundin, J. Catal. 65, 9(1980)
- III. Structural Dynamics of a V_2O_5/SnO_2 Catalyst in the
Ammoxidation of 3-Picoline
A. Andersson, J. Catal. 69, 465(1981)
- IV. Activities of V-Ti-O Catalysts in the Ammoxidation
of 3-Picoline, II. Acid-Base Properties and Infra-
red Spectra
A. Andersson, J. Catal., in press
- V. An Oxidized Surface State Model of Vanadium Oxides
and Its Application to Catalysis
A. Andersson, J. Solid State Chem., in press

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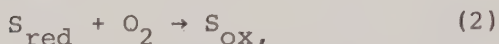
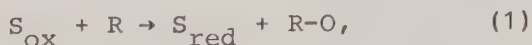
INTRODUCTION

The background for the project on ammoxidation of 3-picoline was an interest from AB Bofors in the early 1970s to manufacture nicotinic acid, or eventually nicotinamide, from 3-picoline by a new route. The process used by the company at that time for production of nicotinic acid was a liquid-phase process, carried out at a high pressure with nitric acid as the oxidizing agent. If air could instead be used as an oxidizing agent, the cost would be lowered and the production simplified. This process was extensively studied at the Department of Chemical Technology at Lund (1). However, from a technical viewpoint the yield of nicotinic acid obtained per single pass through the reactor was not high enough to be of immediate industrial interest. Therefore, an ammoxidation route was considered to be an alternative.

In the 1950s it was reported (2,3) that the reactions of alkyl pyridines with air and ammonia to give nitriles, in the vapour phase, could have an industrial potential. The concept "ammoxidation" was introduced by Hadley (4). The yield of nicotino-nitrile obtained by Mayurnik et al. (3) in the ammoxidation of 3-picoline was 60%. Today it is possible to obtain a yield of about 85-90% (5-7). The ammoxidation of 3-picoline is of interest because of the nitrile may be converted to nicotinic acid by hydrolysis (8,9), or to nicotinamide by catalytic hydration. More than 90% of the nitrile charged can be converted to amide (10-12). Both nicotinic acid and nicotinamide (vitamin B₃) are essential for the nutrition of human beings and animals, and they are used as feed additives. The daily requirement of a human being is around 20 mg of nicotinamide (12). Instead of the amide, the acid can be used because the body has the capability to transform the acid into amide.

The catalysts used in the ammoxidation and oxidation of aromatic hydrocarbons are usually based on promoted and supported vanadium oxides. These catalysts are often referred to as "V₂O₅ catalysts". However, this is not quite correct. The conditions in ammoxidation and oxidation reactions are both re-

ductive and oxidative; i.e., the hydrocarbon consumes oxygen from the catalyst, which is then reoxidized. This can be illustrated as follows:



where S_{ox} is an oxidized form of catalyst, S_{red} is a reduced form, R is a reactant consuming oxygen, and $R\text{-O}$ is a product containing oxygen. It can be expected that under steady-state conditions the catalyst will contain a certain amount of lower oxides formed by reduction of the originally charged catalyst. The degree of reduction depends on the kinetics of the reactions, and varies with the reaction parameters. It follows that the composition of the catalyst will vary through the catalyst bed in a fixed bed reactor. This phenomenon was described by Simard et al. (13), who studied the oxidation of o-xylene to phthalic anhydride.

In the initial stage of the project on the ammoxidation of 3-picoline, the aim was to investigate various catalysts and to optimize the reaction parameters for production of nicotino-nitrile. However, reproducibility problems appeared. When the effect of temperature was studied, different results were obtained depending upon the sequence in which the catalyst temperature was varied in the interval 300-500°C. Higher yields of nicotinonitrile at steady-state were obtained by going from a high to a low temperature, than were obtained by varying the temperature in the reverse manner. It was also observed that the start-up procedure had an influence on activities and selectivities. If the catalyst was exposed to ammonia only, before introduction of air and 3-picoline, an active and especially selective catalyst could be produced. These facts show the importance of what crystal planes are exposed, crystal defects and the presence of reduced phases. It was found that catalysts active and selective in the formation of nicotino-nitrile usually contained V_6O_{13} in addition to V_2O_5 . The early observations induced an increased interest in what really makes

a catalyst active and selective in the ammoxidation of 3-picoline to nicotinonitrile. The outcome of this basic interest is presented in this thesis.

Different opinions about active and selective species on vanadium oxides have appeared in the literature. In the oxidation of propylene, Colpaert (14) concluded that V_2O_5 was not active, V_6O_{13} was active and involved in the selective oxidation, while V_2O_4 had a high activity and favoured complete oxidation to carbon dioxide. Concerning the oxidation of o-xylene to phthalic anhydride, Simard et al. (13) found that the reaction ceased when the catalyst, during the reaction, was reduced to V_2O_4 with a small amount of V_2O_3 . The activity was considered to be limited to V_2O_5 , V_6O_{13} , and to intermediate structures which may exist on the surface. Shaprinkaya et al. (15) studied the oxidation of naphthalene. They found that the catalytic activity in the 380-415°C range decreased in the order: $V_6O_{13} > V_2O_3 > V_2O_4 > V_2O_5$. Contradictory results were obtained by Nishisaka et al. (16). According to these authors, the activity decreased in the order: $V_2O_5 > V_6O_{13} > V_2O_4 (=0)$. Activity studies of different vanadium oxides had not been reported for the ammoxidation of picolines, and those reported for oxidation reactions seemed to include some discrepancies in the results. Therefore, one of the aims of this work was to determine the activity and selectivity of V_2O_5 , V_6O_{13} , and V_2O_4 in the ammoxidation of 3-picoline. The results are given in Paper I. V_2O_3 was not considered because it is not present at steady state under normal operating conditions (13,15).

To vanadium oxide based catalysts, used in the ammoxidation of alkyl pyridines, TiO_2 (17) and SnO_2 (18) are often added as promoters or carriers. Single-promoted vanadium oxide catalysts, V-Ti-O and V-Sn-O, were studied in order to clarify the promoting role of TiO_2 and SnO_2 . The results obtained are presented in Papers II, III and IV.

The origin of the differences in activity and selectivity of V_2O_5 , V_6O_{13} and V_2O_4 must be found in the structure. Paper V deals with the structure of the oxides, and a model of the

surfaces is proposed. The model seems to explain the results of various catalytic investigations of unpromoted vanadium oxides, even though these at first seem contradictory.

METHODS

Apparatus for activity measurements

The apparatus is shown in Fig. 1. Air and ammonia were supplied from pressure cylinders, and the flows were regulated by means of bleed-off tubes and measured on capillary flowmeters. Some of the air passed through a 3-picoline evaporator. The mixture of air, 3-picoline, ammonia, and water vapour was led in heated tubes to a pre-heater before it entered the reactor. Most of the nongaseous products and unreacted 3-picoline were condensed in three condensers, and the rest was absorbed in water absorbers. The temperatures in the condensers were -25°C , -65°C , and -75°C , respectively. Carbon dioxide was absorbed in tubes filled with Ascarite and Dehydrite. Carbon monoxide was oxidized to carbon dioxide in a heated U-tube containing I_2O_5 . After removal of I_2 the dioxide was absorbed on Ascarite-Dehydrite.

Product analysis

The nongaseous products and unreacted 3-picoline were analyzed with a Varian 1200 gas chromatograph (column: 1.5 m, 30% SE-30 on A.W. Chromosorb W). To the column was added 1% TEA to prevent tailing (19) and allow a good separation of nicotinonitrile from 3-pyridinecarboxaldehyde. The oven temperature was 70°C , the carrier gas was nitrogen (20 ml/min), and 2-picoline was used as internal standard. High boiling compounds (tar), eventually formed nicotinic acid and amide were separated from the rest of the condensed reaction mixture by extraction with chloroform and water. The weight of high boiling compounds was determined after evaporation of water under vacuum at 60°C . A mean value of 120 per picoline unit was used for the molecular weight of the high boiling fraction. Carbon dioxide and carbon monoxide, which had first been oxidized to carbon dioxide,

were analyzed by a gravimetric method using tubes filled with Ascarite and Dehydrite. Hydrogen cyanide was determined by means of Dräger tubes.

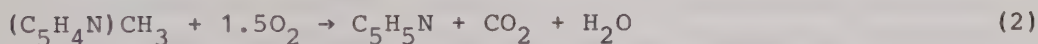
The inlet content of 3-picoline was determined on a Perkin-Elmer F11 gas chromatograph. The 3-picoline was first totally combusted over Fe_2O_3 at 625°C and then analyzed on the chromatograph as carbon dioxide (column: 2.3 m, silica gel). The oven temperature was 110°C , and the carrier gas was helium (21 ml/min).

Reactions

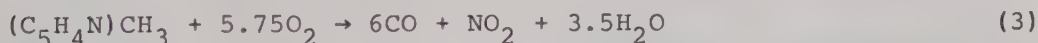
To check the material balance the following reactions were considered. The ΔH -, ΔG - and $\log K$ -values at 400°C are also given.



$$\Delta H_1 = -510.7 \text{ kJ/mole}, \Delta G_1 = -571.3 \text{ kJ/mole}, \log K_1 = 44.3$$



$$\Delta H_2 = -608.3 \text{ kJ/mole}, \Delta G_2 = -644.6 \text{ kJ/mole}, \log K_2 = 50.0$$



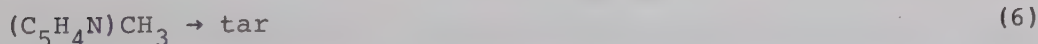
$$\Delta H_3 = -1585 \text{ kJ/mole}, \Delta G_3 = -1988 \text{ kJ/mole}, \log K_3 = 154$$



$$\Delta H_4 = -3287 \text{ kJ/mole}, \Delta G_4 = -3332 \text{ kJ/mole}, \log K_4 = 259$$



$$\Delta H_5 = -2673 \text{ kJ/mole}, \Delta G_5 = -2799 \text{ kJ/mole}, \log K_5 = 217$$



Catalyst preparation

The V_2O_5 catalyst was prepared by heating V_2O_5 powder in a quartz crucible in a high temperature oven for 3 hr at 1150°C . The fused catalyst was divided into small particles, and the 14- to 25- mesh (1.41-0.71 mm) fraction was used in the experiments. The V_6O_{13} catalyst was obtained from the V_2O_5 catalyst by reduction in a hydrogen atmosphere for 1 hr at 450°C . The V_2O_4 catalyst was prepared by heating stoichiometric mixtures of V_2O_5 and V_2O_3 powders in static vacuum at 800°C for 18 hr. The catalyst obtained was a powder with a rather homogeneous particle diameter of about 0.037 mm. The V_2O_3 powder used was obtained by reduction of V_2O_5 powder by hydrogen at 450°C for 20 hr.

The V-Sn-O catalyst and the V-Ti-O catalysts were prepared by heating V_2O_5 and SnO_2 or TiO_2 (anatase) powders for 3 hr at 1150°C . The 14- to 25- mesh fraction was collected and used in the experiments. The V-Ti-O catalysts were pre-reduced in a hydrogen atmosphere for 1 hr at 450°C before activity measurements were performed. In patents it has been described that ammoxidation catalysts can be activated by treatment with ammonia and/or hydrogen (20) or carbon monoxide (21).

Characterization of catalysts

X-Ray diffraction analysis of catalysts was carried out on a Philips X-ray diffraction instrument using a PW 1310/01/01 generator and $\text{CuK}\alpha$ radiation.

The average oxidation number of vanadium was determined by titrimetric methods (22). The samples were dissolved in H_2SO_4 . The degree of reduction was determined by titration with KMnO_4 . The total content of vanadium was subsequently determined by titration with Mohr's salt. Diphenylamine was used as indicator.

SEM investigations were performed with a Jeol JSM-U3 or an ISI-100A scanning electron microscope.

The surface areas of the catalysts were measured with a BET apparatus using N_2 at liquid N_2 temperature. The amounts of irreversibly adsorbed CO_2 and NH_3 at $21^\circ C$ and $200^\circ C$, respectively, were also measured in the BET apparatus.

Infrared spectra of the catalysts were recorded on a Perkin-Elmer 297 or a Perkin-Elmer 580B spectrophotometer. The KBr disc method was used.

SUMMARY OF PAPERS

Paper I: Activities of Vanadium Oxides in Ammoxidation of 3-Picoline.

The experiments were carried out in an integral fixed bed reactor. Each experiment was continued at constant temperature for 40 min, divided into four periods of 10 min. During each period the products and unreacted 3-picoline were collected and then analyzed. Each charge of catalyst was only used at one temperature. The purpose of using catalysts in repeated 10-min periods followed by an integral analysis was that if the periods were short enough and repeated, in this case four times, it should be possible to obtain the activities for the pure oxides by extrapolation to zero time, even though the surface composition changed with time-on-stream. For the different oxides used as catalysts, the temperature was varied while the other parameters were kept constant. The inlet mole ratios air:ammonia:water:3-picoline were 240:13:60:1.

Figure 2a shows the conversion of 3-picoline and the yields of nicotinonitrile, tar and carbon oxides as a function of time-on-stream over V_2O_5 at three temperatures. Both the conversion and the yields were constant during the time the catalyst was examined. This was the case for all the temperatures studied in the interval 300 to $516^\circ C$, allowing extrapolation of all functions to zero time without difficulty. The results indicate that V_2O_5 was the dominant surface phase during the experiments. This conclusion is supported by three other facts.

First, the used and unused catalysts had the same colour. If the catalyst had been permanently reduced to any great extent, the colour would have changed from reddish brown to bluish black or black. Furthermore, the titrimetric method used to estimate the average oxidation number of vanadium did not detect any reduction. Finally, SEM studies did not reveal that any recrystallization had occurred on the surface during the use of the catalyst. All these facts show that the rate of re-oxidation of the catalyst surface is greater than the rate of reduction.

The yield of nicotinonitrile over V_2O_5 had a maximum value of 34% at 458°C. The selectivity of formation of nicotinonitrile was constant, ~60%, at low temperatures. At higher temperatures the nitrile selectivity decreased, and that of carbon oxides and tar increased.

The conversion and the yields as a function of time-on-stream over V_6O_{13} for three temperatures in the interval 285 to 490°C are presented in Fig. 2b. It can be seen that the conversion and the yields of nitrile and tar decreased with time at 285°C. This was the case for all temperatures investigated, up to about 350°C. At higher temperatures the conversion still decreased with time, but the yield of the nitrile began to increase. The higher the temperature, the less significant became the decrease of the conversion and the more significant became the increase of the yield of nitrile. The average oxidation number of vanadium was also determined. The oxidation number had increased, especially after the catalyst had been used at higher temperatures. The X-ray diffraction patterns of used catalyst were registered, showing the presence of V_6O_{13} , V_2O_5 and very small amounts of V_2O_4 . A comparison of the data on V_2O_5 and V_6O_{13} presented in Fig. 2, allows the conclusion that the activity of V_6O_{13} is higher than that of V_2O_5 . Thus, the results obtained for the V_6O_{13} catalyst at temperatures below 350°C (See 285°C in Fig. 2a) can be explained by the V_6O_{13} surface being oxidized to V_2O_5 . At 285°C the selectivity for formation of nitrile was about 60% throughout the experiment. This is expected, since the selectivities of V_6O_{13} and

V_2O_5 are about the same at lower temperatures. The measured increase of the selectivity for the nitrile at temperatures above 350°C is, however, remarkable. At 380°C , where the formation of carbon oxides was negligible, the selectivity increased from 79 to 93% during 40 min. At 490°C , where in the beginning the oxidation to carbon oxides was rather important, the selectivity increased with time-on-stream from 21 to 70%. These results cannot be explained by independent phase contributions from the V_6O_{13} and V_2O_5 phases, which is possible for results obtained at lower temperatures. It is probable that the formation of new phases creates phase boundaries and that the extent of these boundaries increases with the temperature. If the boundaries are active and especially more selective than the pure oxides, this will explain the high temperature results. The reason for the amount of phase boundaries to increase with temperature is that the oxygen mobility in the catalyst and the rate of oxygen diffusion increases with temperature. This leads to the creation of a large amount of very small V_2O_5 domains on the V_6O_{13} surface. This explanation is strengthened by published results. It has been shown (23,24) that reduced V_2O_5 was oxidized only in the surface layer at temperatures below 200°C . At 300°C the oxidation also occurred in the bulk. The results obtained for the V_6O_{13} catalyst indicate a surface layer oxidation at a somewhat higher temperature ($<350^\circ\text{C}$), which can depend on the fact that during the ammoxidation both reduction and oxidation of the catalyst occur simultaneously. The kinetics of the exchange of oxygen ^{18}O between the gaseous phase and V_2O_5 has been studied. The results have shown (25) that above $\sim 400^\circ\text{C}$ the rate-limiting step is the exchange across the surface and that the diffusion of bulk oxygen towards the surface is faster than the surface exchange.

Over the V_6O_{13} catalyst the yield of nicotinonitrile had a maximum, 76%, at 365°C . The conversion was 98%.

Results obtained over the V_2O_4 catalyst are shown in Fig. 2c. The conversion and the yields which can be noticed after extrapolation to zero time are probably due to the V_2O_5 phase which was originally present in the fresh catalyst. The average

oxidation number of vanadium in the unused catalyst was 4.10, and X-ray diffraction analysis showed the presence of a small amount of V_2O_5 . The conclusion is that V_2O_4 is not active. This seems reasonable because the conversion over the V_2O_4 catalyst at 451°C was only 2.5%. The conversion over the V_2O_5 catalyst under the same experimental conditions was around 55%. Therefore, the low conversion over the V_2O_4 catalyst can be attributed to the small amount of V_2O_5 that was present.

Figure 2c shows that the conversion and the yield of nicotino-nitrile increased with time-on-stream. The V_2O_4 catalyst was examined by X-ray diffraction. In catalyst used between 353 and 451°C only V_2O_4 and V_2O_5 could be detected. In the catalyst used at 502°C V_6O_{13} could also be identified. The ratios of the peaks with the highest intensities for this catalyst were $V_2O_5:V_2O_4=0.07$ and $V_6O_{13}:V_2O_4=0.15$. Titrimetric analysis showed that the average oxidation number of vanadium had increased from 4.10 to 4.28 during 40 minutes of use. The appearance of higher oxides must be the explanation for the increasing conversion and yield of nitrile.

Furthermore, a mechanism for the formation of nicotinonitrile is proposed, which includes a step in which an adsorbed aldehyde complex reacts with ammonia.

Paper II: Activities of V-Ti-O Catalysts in the Ammoxidation of 3-Picoline.

The V-Ti-O catalysts were pre-reduced. X-ray diffraction analysis of fresh catalysts showed that of the vanadium oxides, V_6O_{13} was the major phase. The conversion and the yields of nicotinonitrile, carbon oxides, and tar were analyzed as a function of time-on-stream. For catalysts containing 10-70 mole % TiO_2 the conversion decreased with time. At higher temperatures the decrease was not so pronounced. The yield of nicotinonitrile also decreased strongly at temperatures around 300°C . At temperatures above 350°C , on the contrary, the yield of nicotinonitrile increased with time-on-stream. Concerning tar and carbon oxides, the yields decreased with time-on-stream at all temperatures in-

investigated. The influence of time was virtually the same for catalysts with 10-70 mole % TiO_2 as well as for the V_6O_{13} catalyst with no TiO_2 (See Paper I). From X-ray diffraction analysis and trimetric estimations of the average oxidation number of vanadium in used catalysts, it follows that the catalysts were oxidized during the ammoxidation process. It is proposed in Paper I that the influence of time-on-stream at low temperatures on a V_6O_{13} catalyst can be explained by oxidation of the catalyst surface to V_2O_5 , which is less active than V_6O_{13} . It was also found that the results at high temperatures could not be explained by separately acting V_2O_5 and V_6O_{13} phases. These results were discussed in terms of the formation of boundary surfaces between V_2O_5 and V_6O_{13} , which must be more selective than any separate phase. Therefore, in view of results obtained for catalysts with 10-70 mole % TiO_2 , it seems reasonable to suggest the same explanation in this case, i.e., separately acting TiO_2 -promoted V_6O_{13} and V_2O_5 at low temperatures, and the formation of selective boundary surfaces between the TiO_2 -promoted vanadium oxides at high temperatures.

The results for the catalyst with 90 mole % TiO_2 were different in that the yield of nicotinonitrile decreased with the reaction time at all temperatures investigated. An explanation for this can be that V_6O_{13} is present only as a thin layer on the TiO_2 phase, which has no bulk capacity for oxygen. This means that boundary surfaces between promoted V_2O_5 and promoted V_6O_{13} cannot be formed to any great extent.

To compare the activities related to the initial composition of the catalysts, the rate constants at different temperatures were calculated. The data were obtained by extrapolating the conversion and yields to time zero. It was assumed that the reaction scheme could be approximated by first-order reactions in a limited interval of temperature, where the main product was nicotinonitrile and only minor amounts of tar and practically no carbon oxides were formed. The initial reaction rates as a function of the TiO_2 content are given in Fig. 3. It is seen that the activity has a maximum at 50-60 mole % TiO_2 . Concerning

the selectivity of nicotinonitrile on the different catalysts, it is of interest to compare them at a high conversion, the same mole ratios for the reactants and at the same temperature. In Fig. 4 the selectivities of nicotinonitrile, related to fresh catalyst composition, are compared at 90% conversion. The temperature was 320-328°C. The selectivity varies between 73 and 83%, with a maximum at 10 mole % TiO_2 and a minimum at 30 mole % TiO_2 . At larger TiO_2 contents, the selectivity increased continuously.

To clarify the promoting role of TiO_2 further investigations of the pre-reduced V-Ti-O catalysts were carried out. These results are presented in Paper IV.

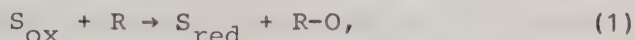
Paper III: Structural Dynamics of a $\text{V}_2\text{O}_5/\text{SnO}_2$ Catalyst in the Ammoxidation of 3-picoline.

One of the objects of this investigation was to study how the conversion and the selectivity of formation of nicotinonitrile depend on the reaction parameters in the ammoxidation of 3-picoline over a V-Sn-O catalyst (V:Sn = 2:1.5). The highest yield of nicotinonitrile was 82% at 98% conversion. This was obtained at 400°C, with a space velocity of 4000 h^{-1} and the following mole ratios: ammonia/3-picoline = 12, air/3-picoline = 210, and water vapour/3-picoline = 40.

The dynamic structure of the catalyst surface was studied by determining the phases present by X-ray diffraction analysis and the average oxidation number of vanadium by titrimetric methods. All the measurements were made under steady-state conditions. Table 1 shows the effect of the reaction parameters on the average oxidation number of vanadium. The composition obtained by X-ray diffraction analysis of the first 2 ml of the catalyst bed at the reactor inlet is summarized in Table 2.

Experiments 10, 2 and 8 show the influence of increasing temperature. At 406°C, the value of the oxidation number shows that the catalyst has been oxidized, as compared to the freshly prepared catalyst (ON = 4.88 ± 0.01). On the contrary, at 459°C the first 0.7 ml of the catalyst bed has a lower oxidation

number than the unused catalyst. This reduction is in agreement with the X-ray data presented in Table 2, which show that V_6O_{13} could be detected. The degree of reduction of the catalyst under steady-state conditions depends on the kinetics of the following two types of reaction:



where S_{ox} is an oxidized form of catalyst, S_{red} is a reduced form, R is a reactant consuming oxygen, and R-O is a product containing oxygen. Depending on the rate constants and the activation energies of the above reactions, the fact that the average oxidation number of vanadium varies with temperature can be understood.

If the data in Tables 1 and 2 for Expts. 2 and 16 are compared it seems that an increase in the partial pressure of ammonia causes a small increase in the degree of the reduction of the catalyst. However, it was found that the conversion is constant over a wide range of partial pressures of ammonia, and that the yield of nicotinonitrile increases with the partial pressure of ammonia. Thus it seems that the increased degree of reduction of vanadium cannot be caused by a great increase in the oxygen consumption by the hydrocarbons. However, it is possible that the increased reduction can be caused by oxidation of ammonia to nitrogen and water, which is known to occur on vanadium oxide catalysts (26). The increase of the selectivity can be seen as a consequence of the increased degree of reduction. The conclusion was drawn (Papers I and II) that coherent boundaries between V_2O_5 and V_6O_{13} are especially selective in the ammoxidation of 3-picoline. From the X-ray data given in Table 2 it can be concluded that the amount of V_6O_{13} is greater in the catalyst being used under a higher ammonia partial pressure.

If a comparison between Expts. 449 and 16 is made, it is seen that in the former the partial pressure of oxygen was lower and the partial pressures of the oxygen-consuming components 3-picoline and ammonia were higher. The decrease in the partial pressure of oxygen gives a lower conversion (Table 1), which shows the importance of the partial pressure of oxygen on the reaction rates. In Expt. 449 the degree of reduction compared to Expt. 16 seems to be somewhat higher in spite of a lower conversion. This can depend on an increase of the amount of ammonia converted to nitrogen.

In Expts. 10 and 449 the magnitude of the conversion was the same, but the selectivity of formation of the nitrile was greater in Expt. 449. This is reflected in a more reduced catalyst (Table 2) and in the formation of V_6O_{13} , which again shows the importance of V_2O_5/V_6O_{13} boundaries in obtaining a high selectivity.

Experiment 450 was performed without the addition of water vapour. In comparison with Expt. 16 it is seen that, in spite of the higher partial pressures of oxygen, ammonia, and 3-picoline used in Expt. 450, the conversion and the selectivity of nicotinonitrile are lower. Also, the degree of reduction of vanadium was greater in the case without water vapour addition, especially in the first part of the catalyst bed, which had become black. An explanation of these results could be that some of the vanadium is reduced to V_2O_4 (Table 2), which was found to be inactive in the ammoxidation of 3-picoline (Paper I). The lower selectivity can depend on the fact that the amount of coherent V_2O_5/V_6O_{13} boundaries decreases as some of the vanadium is reduced to V_2O_4 .

The results discussed so far show the applicability of the basic knowledge of vanadium oxides presented in Paper I to a promoted system under steady-state conditions. However, it is also of importance to clarify the promoting role of SnO_2 .

ESCA investigations of a similar V_2O_5/SnO_2 catalyst have shown that the surface concentration of V_2O_5 is higher than the

stoichiometric bulk composition (27). This is because the SnO_2 particles are embedded in a matrix of V_2O_5 . Therefore, the conclusion can be drawn that only the vanadium oxide phase is exposed and that this is the real catalyst. Infrared investigations of the catalyst showed that the band ascribed to the stretching vibrations of the short $\text{V}=\text{O}$ bonds in V_2O_5 , has shifted its position from 1025 cm^{-1} in pure V_2O_5 to 1020 cm^{-1} in the catalyst. This shift indicates that the short $\text{V}=\text{O}$ bonds in the V-Sn-O catalyst are weaker than those in V_2O_5 . The weakening can be seen as a consequence of the incorporation of Sn^{4+} in the V_2O_5 lattice. It has been found (28) that V_2O_5 , in the molten state, can dissolve various ions. This dissolution leads to a loss of oxygen, which explains why the oxidation number of vanadium was less than +5 in freshly prepared catalyst. The weakening of the $\text{V}=\text{O}$ bonds leads to a greater ability to form active and selective $\text{V}_2\text{O}_5/\text{V}_6\text{O}_{13}$ boundaries in the catalyst during its use in the ammoxidation process. In the absence of SnO_2 , no reduction of V_2O_5 could not be detected under the same experimental conditions (Paper I).

X-Ray diffraction analysis of the catalyst revealed a small shift of the SnO_2 lines in the back-reflection region compared to pure SnO_2 . This shift is caused by a change in the lattice parameters of the SnO_2 phase, which depends on the presence of dissolved V^{4+} . Sachtler et al. (29) used the ESR technique to show that the SnO_2 lattice is capable of dissolving tetravalent vanadium. Chemical analysis of the catalyst gave the composition of the SnO_2 phase as $\text{V}_{0.03}\text{Sn}_{0.97}\text{O}_2$.

Paper IV: Activities of V-Ti-O Catalysts in the Ammoxidation of 3-Picoline; II: Acid-base properties and infrared spectra.

Results concerning the ammoxidation of 3-picoline on pre-reduced V-Ti-O catalysts were presented in Paper II. However, it seemed necessary to gain further information on the nature of the variation of activity and selectivity with the TiO_2 content. The methods used were determination of the acidic and basic

properties and infrared investigations of the catalysts.

The amount of irreversibly adsorbed NH_3 at 200°C was used as a measure of the acidity. The results are collected in Table 3. It is obvious that catalysts with a high concentration of acidic sites, 0, 10 and 90 mole % TiO_2 , also have a low activity. Furthermore, a high activity tends to correspond to a lower acidity. However, the relation in the interval 30-70 mole % TiO_2 is somewhat irregular. This shows that other factors are also of importance, e.g. the vanadium-oxygen bond strength and the concentration of active species. The correlation between a high acidity and a low activity indicates that the measured acidity can be considered to be a measure of the -OH group concentration. The amount of adsorbed 3-picoline is low at a high concentration of -OH groups because these groups have no ability to adsorb 3-picoline. It has been observed (30) that NH_3 on V_2O_5 , up to about 150°C , is adsorbed as NH_4^+ (ad), and that the quantity of -OH groups was not affected by oxidation or evacuation treatment at $400\text{-}500^\circ\text{C}$ (31). These groups can act as adsorption sites for NH_3 at high temperatures, even though the adsorbed quantity is too small to be detectable by infrared absorption because of the low transmittance of vanadium oxides.

In the exchange of oxygen between CO_2 and V_2O_5 at 370°C it has been proposed (32) that CO_2 is dissociatively chemisorbed at a special site on the surface, composed of a vanadyl group and a vacant vanadium atom. These species were assumed to be easily convertible to other forms like a bridge type of adsorption and chemisorption of a CO_2 molecule on a surface oxygen atom. During the pre-reduction of the catalysts, lower oxides were formed, and probably oxygen vacancies as well. These defects are surrounded by surface oxygen atoms. It was thought that the vacancies could be measured by adsorbing CO_2 at room temperature. At this temperature the bridge type of adsorption can be excluded because oxygen exchange between CO_2 and the vanadium oxide does not occur. The values of the amount of irreversibly adsorbed CO_2 at 21°C are given in Table 3. It seems clear that the measured surface basicity can be corre-

lated with the selectivity of formation of nicotinonitrile. The correlation can be understood if the basicity is a measure of vacancies close to active oxygen species. The existence of vacancies diminishes the possibility of complete oxidation to carbon oxides.

The infrared spectra of the pre-reduced V-Ti-O catalysts in the range $950\text{--}1050\text{ cm}^{-1}$ are shown in Fig. 5. The initial activity and selectivity of these catalysts are those values given in Table 3. It is obvious that a shoulder appears on the low wavenumber side of the V_2O_5 peak. The V_2O_5 spectrum was subtracted, and the difference spectra obtained are presented in Fig. 5b. These spectra show the existence of a band between 960 and 1020 cm^{-1} with a maximum around 995 cm^{-1} . The catalyst with 90 mole % TiO_2 also exhibits the same band, but no V_2O_5 peak. The only phases in the catalysts which could be identified by XRD were V_2O_5 , V_6O_{13} , V_2O_4 and TiO_2 , but the band around 995 cm^{-1} was not found in the spectra of these oxides. The same band, however, appeared in the spectrum of a homogeneous $\text{V}_2\text{O}_5/\text{V}_6\text{O}_{13}$ mixture, which was obtained by decomposing NH_4VO_3 at 700°C in a nitrogen atmosphere. During the decomposition NH_3 , which is a reducing agent, was evolved throughout the bulk of the material. Therefore, it is assumed that the new band observed is due to $\text{V}_2\text{O}_5/\text{V}_6\text{O}_{13}$ boundaries. Such boundaries were found to be active and selective in the ammoxidation of 3-picoline (Papers I-III). The nature of the boundaries is not known. It has been demonstrated that sharp coherent $\text{V}_2\text{O}_5/\text{V}_6\text{O}_{13}$ boundaries can be formed, because of a structural fit (33). Even though a crystallographic fit exists, it is possible that the boundary is not a sharp border but a transition region. Several oxides and defect structures with a composition between V_2O_5 and V_6O_{13} have been reported (34). Some of these structures have been proposed to contain ordered oxygen vacancies.

The X-ray diffraction patterns of the catalysts did not agree with any of those given in the literature for oxides with a composition between V_2O_5 and V_6O_{13} . Except for the lines due to V_2O_5 , V_6O_{13} , V_2O_4 and TiO_2 , only a few additional weak

lines were found. Their position varied from one sample to another. Also, the difference spectrum in Fig. 5b was not identical with the spectra for VO_2 (A), VO_2 (B), V_4O_9 or vanadium oxide hydrates (35). A peak at 1035 cm^{-1} due to monomeric $(\text{V}=\text{O})^{3+}$ stretching vibrations in VOCl_3 has been reported (36). The stretching frequencies of $(\text{V}=\text{O})^{2+}$ units in a number of compounds have been found in the interval $955\text{--}978\text{ cm}^{-1}$ (37). Therefore, it is concluded that the band around 995 cm^{-1} in the catalysts can be due to a V_2O_5 phase with a number of disordered vacancies in the lattice or a nonstoichiometric V_6O_{13} phase. The shift of the $\text{V}=\text{O}$ frequency from that for $(\text{V}=\text{O})^{3+}$ towards that for $(\text{V}=\text{O})^{2+}$ can thus be related to a decrease of $p_\pi\text{--}d_\pi$ oxygen-metal interactions and an increased electrostatic repulsion of the vanadium and oxygen species.

The composition of the vanadium oxide phase in the catalyst is presented in Fig. 6, which shows that the amount of V_2O_4 increases with the TiO_2 content. It has been observed (38) that a relatively weak band appeared at about 1000 cm^{-1} in the IR spectrum of nonstoichiometric V_2O_4 . It was assumed that this band may be caused by $(\text{V}=\text{O})^{3+}$ stretching vibrations. Therefore, it seems possible that the new band observed at 995 cm^{-1} is due to two defects: i) a nonstoichiometric V_2O_5 or V_6O_{13} phase at low TiO_2 contents and ii) an increasing amount of a nonstoichiometric V_2O_4 phase at higher TiO_2 concentrations.

Due to the weakening of the $\text{V}=\text{O}$ bond, the band at 995 cm^{-1} can be considered to be a measure of activity, provided all the species are located on the surface. This is not completely the case, but because they are located at the outer parts of the catalysts, these oxygens may affect the catalytic activity. The relative amount per surface area was calculated. These values are plotted in Fig. 7, which shows that the amount increases with the TiO_2 content. In conjunction with a low concentration of --OH groups on the surface, this can be essential for the increasing activity, which has been observed for a TiO_2 content up to 50 mole % (Table 3). The low activity of the 90 mole %

TiO_2 catalyst depends on the high concentration of $-\text{OH}$ groups on the surface. Another fact of importance is the possibility that the surface is largely covered with V_2O_4 , which was found to be inactive (Paper I).

The band in the difference spectrum in Fig. 5b has the same position whether TiO_2 is present or not. Also, the degree of reduction increases with the TiO_2 content. These results can be explained by considering the work of Clauws and Vennik (39,40), who found a defect in V_2O_5 crystals by studying the optical absorption. This defect was attributed to oxygen vacancies. The same near-infrared spectrum was obtained for TiO_2 -promoted V_2O_5 crystals, but the intensity was greatly enhanced. This effect was explained by the incorporation of Ti^{4+} into V_2O_5 , which was compensated by the creation of oxygen vacancies. A vanadium ion adjacent to the vacancy may localize an excess electron. This would lead to increased formation of V^{4+} . The catalysts used in the ammoxidation were prepared by heating V_2O_5 and TiO_2 at 1150°C . At this high temperature Ti^{4+} is dissolved in the V_2O_5 melt and V^{4+} species are formed. These species weaken the $\text{V}=\text{O}$ bonds due to increased electrostatic repulsion of the vanadium and oxygen ions. The amount of V^{4+} species probably increases with the TiO_2 content, since the contact area between the molten V_2O_5 and the TiO_2 particles increases. The increase in the amount of V^{4+} , as well as weak $\text{V}=\text{O}$ groups, result in an increased degree of reduction during the H_2 treatment of the catalysts. This explains Fig. 6. It also to some extent explains the results in Table 3, concerning the amount of irreversibly adsorbed CO_2 as a function of the TiO_2 content. The increase of $(\text{CO}_2)_{\text{irr}}$ from 0 mole % to 10 mole % TiO_2 might be caused by an increase in the number of oxygen vacancies. The minimum at 30 mole % TiO_2 can be due to elimination of vacant sites by shear. It has been proposed (41,42) that shear is likely to occur if the concentration of vacancies becomes too great. The final increase of $(\text{CO}_2)_{\text{irr}}$ from 30 mole % to 90 mole % TiO_2 can then be considered to be

due to an increased concentration of vacancies in the shear structure.

Paper V: An Oxidized Surface State Model of Vanadium Oxides and Its Application to Catalysis.

The charge distribution around the V-O bonds in V_2O_5 , V_6O_{13} and V_2O_4 was calculated by using the empirical formula: $d = 1.791 - 0.722 \log_{10} s$, where d is the individual bond length and s is the electron delocalization around the individual bond. The formula was derived for vanadium oxides (43), and is based on the logarithmic relationship given by Pauling (44). The same method can be used to calculate cation-oxygen bond valences in other compounds (45).

In this paper, the surfaces of lower oxides were treated as though they were in an oxidized state, which is believed to correspond to the conditions in oxidation and ammoxidation processes. ESCA investigations of lower vanadium oxides (46) have shown that these oxides contain V^{5+} on the surface. Only a combination of a high vacuum and a high temperature gave surfaces in close agreement with the stoichiometry. It is anticipated that the equation used to calculate the charge distribution between vanadium and oxygen in the bulk is still valid at a solid surface exposing 1-coordinated anions. This seems reasonable because the formula can be used to calculate the charge distribution around 2-, 3-, and 4-coordinated anions in the bulk. In these cases, the electron delocalization around each V-O bond is in practice calculated as though the anion may be considered to be 1-coordinated. The V-O bond lengths at the V_2O_5 surface can be approximated with the values valid for the bulk because the V^{5+} ions at the surface cannot donate any further electrons. However, the bond lengths on the surfaces of V_6O_{13} and V_2O_4 differ considerably from those in the bulk, since the vanadium ions in these oxides are not in the highest possible oxidation state. Therefore, they can donate more electrons to the oxygen species, which leads to a shortening of the V-O surface bonds.

It is generally accepted that for V_2O_5 catalysts the double bonded oxygen in the (010) plane plays a role in catalytic oxidation reactions (47-50). Therefore, it is of interest to locate such groups at surfaces. The result of the calculations is that in V_2O_5 the V=O groups are located on the (010) plane, while in V_6O_{13} they are mainly located on the (001) surface plane. The concentration of V=O groups on V_2O_5 and V_6O_{13} surfaces can be as high as 8.1 and 15.1 $\mu\text{mole/m}^2$, respectively. In V_6O_{13} each double bonded oxygen on the (001) plane belongs to a VO_6 octahedron, which shares edges with two other octahedra having double bonded oxygens. This gives extremely short distances between the active species, which is not the case for V_2O_5 . In V_6O_{13} the (100) plane, according to the model, also has some V=O groups. All these facts together can explain why V_6O_{13} was found to have a higher activity than V_2O_5 (Paper I). In V_2O_4 , V=O bonds are located on the crystallographically equal (100) and (010) planes. Their activity is probably severely limited by steric hindrance, because they are essentially lying in the plane. This is not the case for V_2O_5 and V_6O_{13} surfaces, where the V=O bonds are directed perpendicularly out of the surface. This can be the reason why V_2O_4 was found to be inactive (Paper I). However, the V_2O_4 (110) plane has oxygens directed perpendicularly out of the surface. A limitation of their activity can be the fact that they lie in rows with a long distance of 6.4 Å between the rows.

Surface anions with a valence around -1 can be considered to represent stable OH^- groups because, otherwise, they are strongly undersaturated (43). If the valence of the anion is considerably less than -1, its position can be assumed to be vacant at the high temperatures used in oxidation and ammoxidation processes. In this case the vacancy will be localized at a vanadium ion with a valence above +4. This indicates that the reoxidation rate is relatively slow in comparison with the vacancy is localized at a V^{3+} ion (24), which will be the case after a double bonded oxygen has reacted.

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TABLE 1

Effect of Reaction Parameters on the Average Oxidation Number of Vanadium

Expt. No.	T (°C)	P_O/P_p (P_O (kPa))	P_N/P_p (P_N (kPa))	P_H/P_p (P_H (kPa))	P_p (kPa)	V (cm/s)	ON ^{a)}	Conver- sion (%)	Selec- tivity (%)
10	355	212 (82.6)	3.0 (1.11)	44 (17.1)	0.385	6.3	4.89	48	85
2	406	220 (82.3)	3.0 (1.11)	47 (17.5)	0.375	6.8	4.92	96	73
8	459	212 (82.7)	2.8 (1.11)	44 (17.1)	0.385	7.4	4.83 (0-0.7 cm ³) 4.91 (0.7-2 cm ³)	99.6	39
16	403	214 (76.1)	11 (3.95)	59 (21.0)	0.355	7.0	4.89	92	88
448	401	219 (77.0)	12 (4.26)	56 (19.7)	0.355	5.0	4.88	99.9	45
449	399	97 (57.4)	12 (7.09)	61 (36.2)	0.598	7.2	4.87	45	93
450	400	219 (95.6)	12 (5.27)	0 (0)	0.436	7.0	4.76 (0-1 cm ³) 4.91 (1-2 cm ³)	89	73

T = Reaction temperature. P_O , P_p , P_N , and P_H are the inlet partial pressure of air, 3-picoline, ammonia and water vapour, respectively. V = Linear inlet gas velocity at reactor temperature.

ON = Average oxidation number of vanadium.

a) Unless otherwise noted, the values given are a mean value for the first 2 ml of catalyst at the reactor inlet.

b) Values obtained with 8 ml of catalyst.

TABLE 2

X-Ray Investigation of Phases Present in Catalysts
at Steady State

Expt. No.	Phases (Intensities ^a)			
	SnO ₂	V ₂ O ₅	V ₆ O ₁₃	V ₂ O ₄
10	vs	vs	-	-
2	vs	vs	-	-
8 (0-0.7 cm ³)	vs	vs	vw	-
(0.7-2 cm ³)	vs	vs	vw	-
16	vs	vs	vw	-
448	vs	vs	vw	-
449	vs	vs	vw	-
450 (0-1 cm ³)	vs	vs	vw	vw
(1-2 cm ³)	vs	vs	vw	-

^a vs: very strong; vw: very weak; -: not detectable

TABLE 3

Initial Reaction Rate, Selectivity, Acidity and Basicity

Reaction Parameters: Mole ratio air: 3-picoline: $\text{NH}_3:\text{H}_2\text{O} = 245:1:14:60$. Temp = 320°C . Pressure = 101 kPa					
Catalyst (mole % TiO_2)	Specific Surface Area (m^2/g)	r_{O_2} ($\mu\text{mole}/\text{m}^2\cdot\text{min}$)	Sel. (%) of Nitrile	$(\text{NH}_3)_{\text{irr}2}$ ($\mu\text{mole}/\text{m}^2$)	$(\text{CO}_2)_{\text{irr}2}$ ($\mu\text{mole}/\text{m}^2$)
0	9.4	1.34	73.5	2.95	0.36
10	13.2	1.37	83	2.63	1.99
30	10.7	1.34	75.5	0.24	0.12
50	4.0	3.65	80	1.05	0.49
70	3.8	3.33	78.5	0.48	0.65
90	1.5	0.64	84.5	2.97	1.15

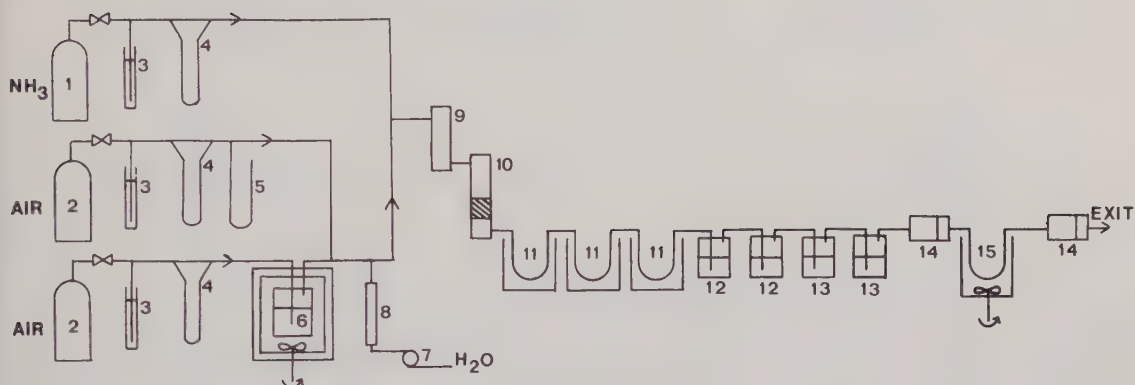


Figure 1. Apparatus for investigation of ammoxidation of 3-picoline. 1, Ammonia cylinder; 2, air cylinder; 3, bleed-off tube; 4, flowmeter; 5, manometer; 6, 3-picoline evaporator; 7, pump; 8, water evaporator; 9 preheater; 10, reactor; 11, condenser; 12, water absorber; 13, H_2SO_4 absorber; 14, Ascarite-Dehydrite; 15, I_2O_5 .

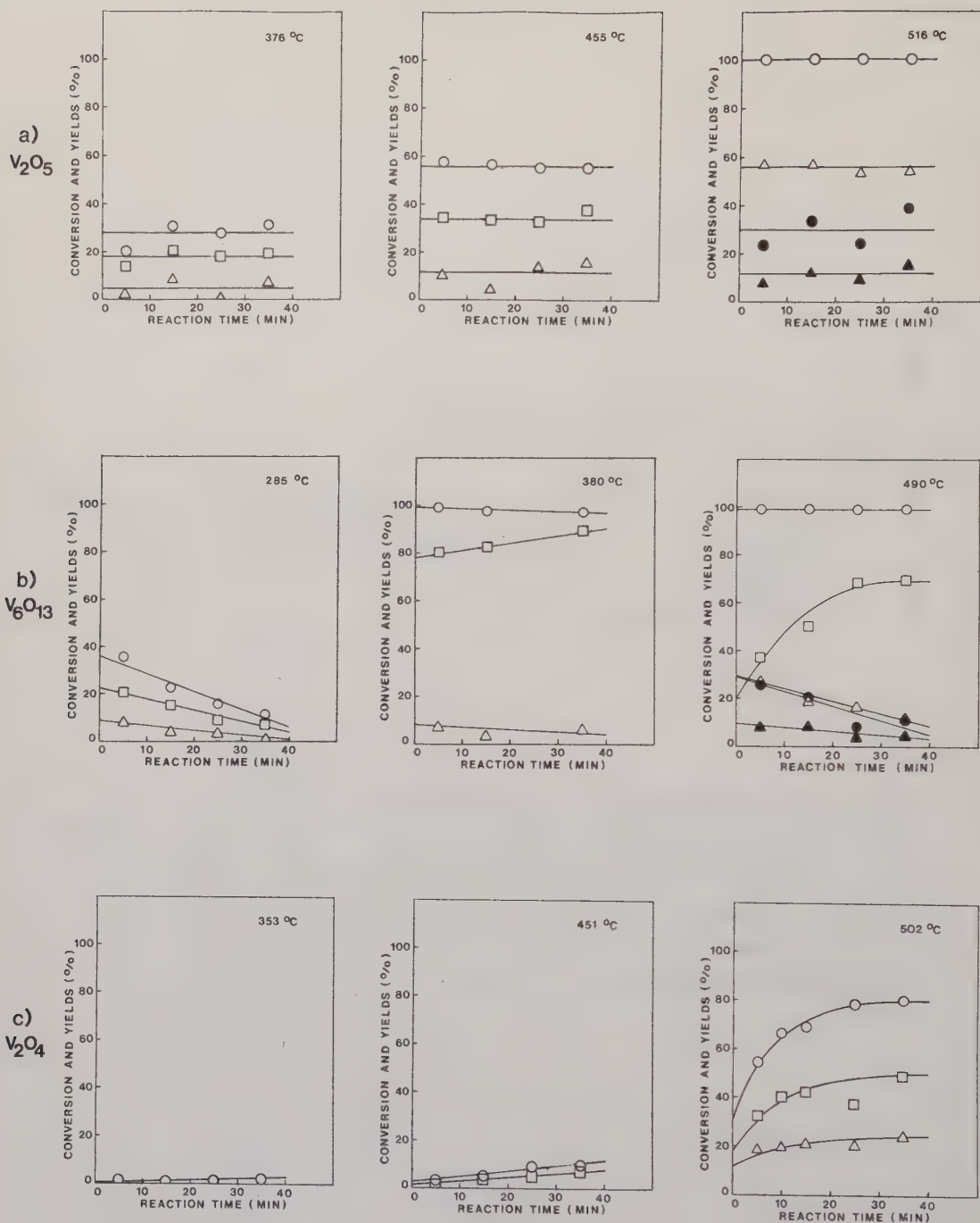


Figure 2. Conversion and yields on a) V_2O_5 , b) V_6O_{13} , and c) V_2O_4 catalysts as a function of time-on-stream.

o = conversion, $\square$ = yield of nicotinonitrile, Δ = yield of tar, $\bullet$ = yield of carbon dioxide, and $\blacktriangle$ = yield of carbon monoxide. Mole ratio air: ammonia: water: 3-picoline = 240:13:60:1, and $A/F = 110 \text{ cm}^2 \cdot \text{sec}/\mu\text{mole}$.

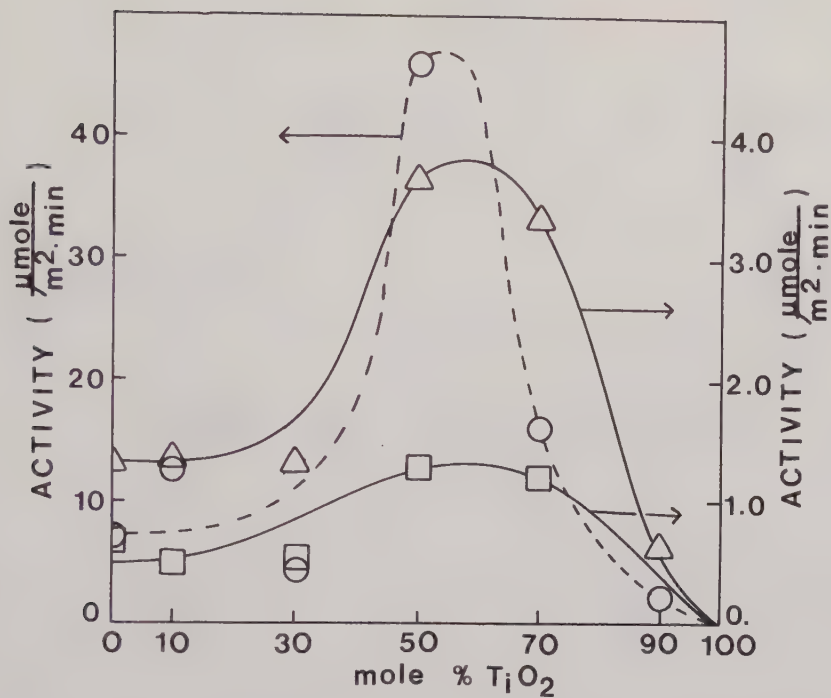


Figure 3. Activities as a function of the TiO_2 content.

Δ = Initial reaction rate at 320°C , $\square$ = average reaction rate (0-90% conv.) at 320°C , and o = initial reaction rate at 380°C .

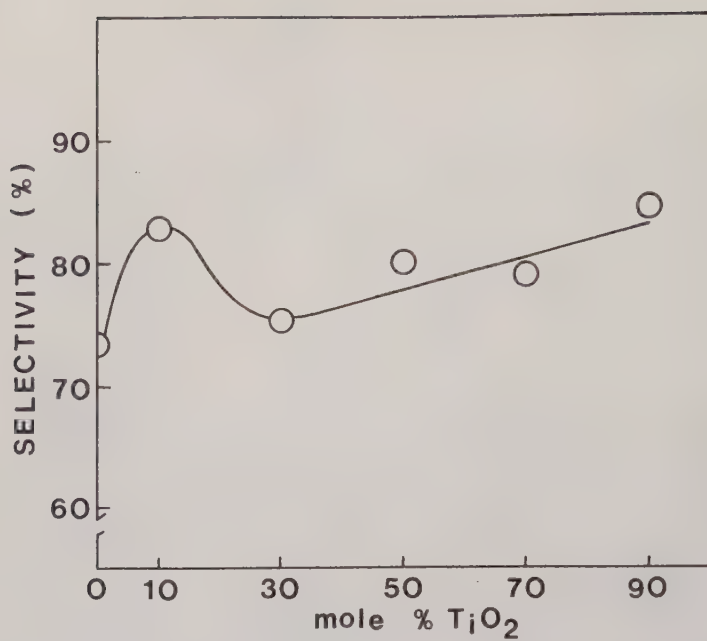


Figure 4. The selectivity of nicotinonitrile as a function of the TiO_2 content (90% conv., and 320-328°C).

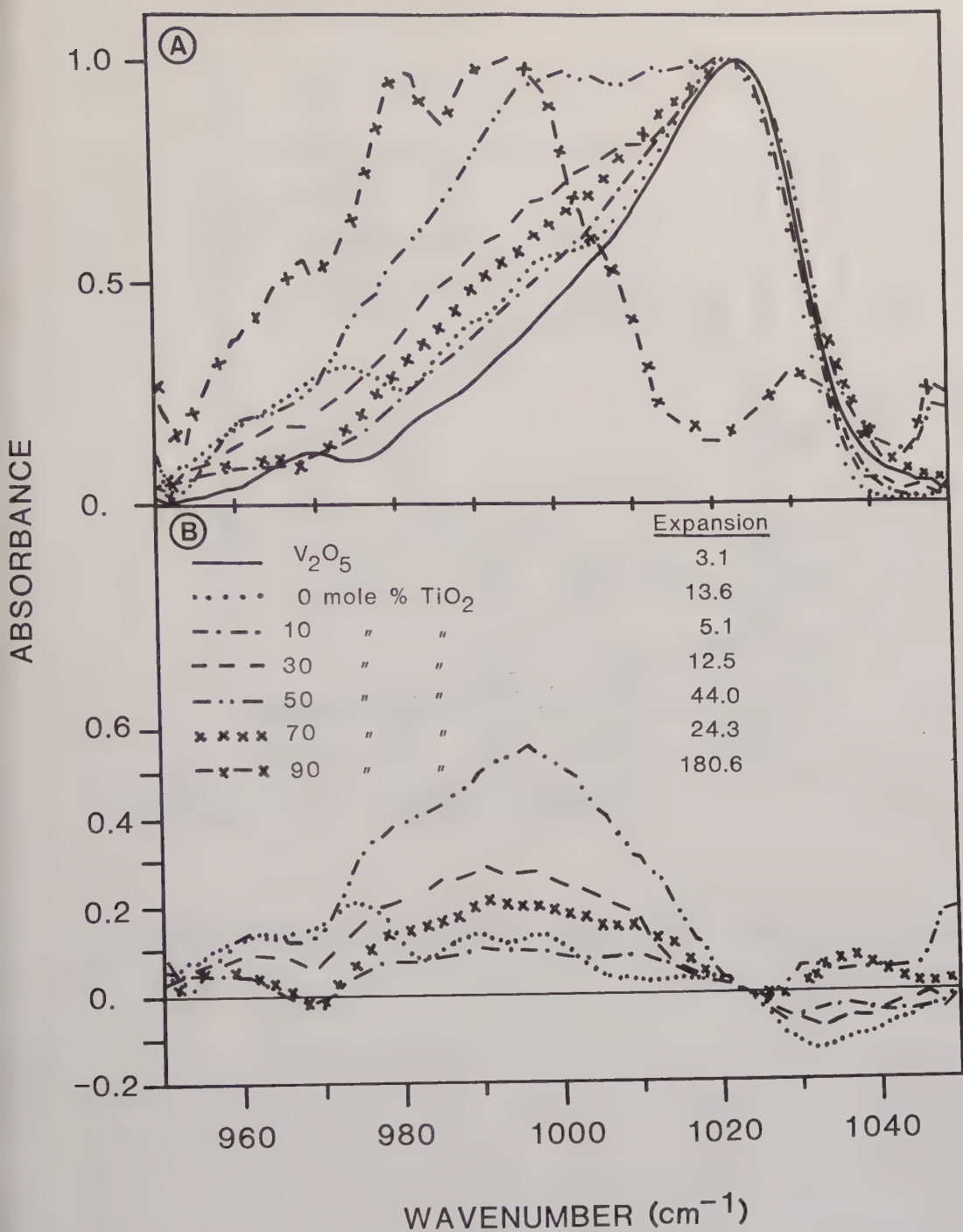


Figure 5. A: Infrared spectra of V_2O_5 and pre-reduced catalysts. 1 mg sample. The strongest peak has been expanded to the absorbance equal to 1.0. B: Resulting absorbance after subtraction of the V_2O_5 absorbance.

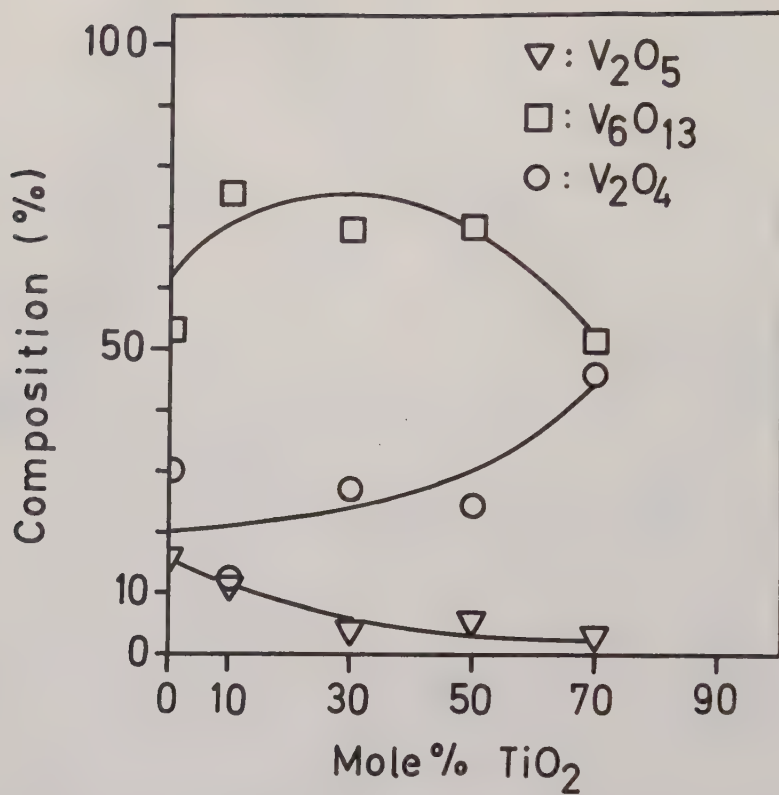


Figure 6. Vanadium oxide composition in pre-reduced catalysts.

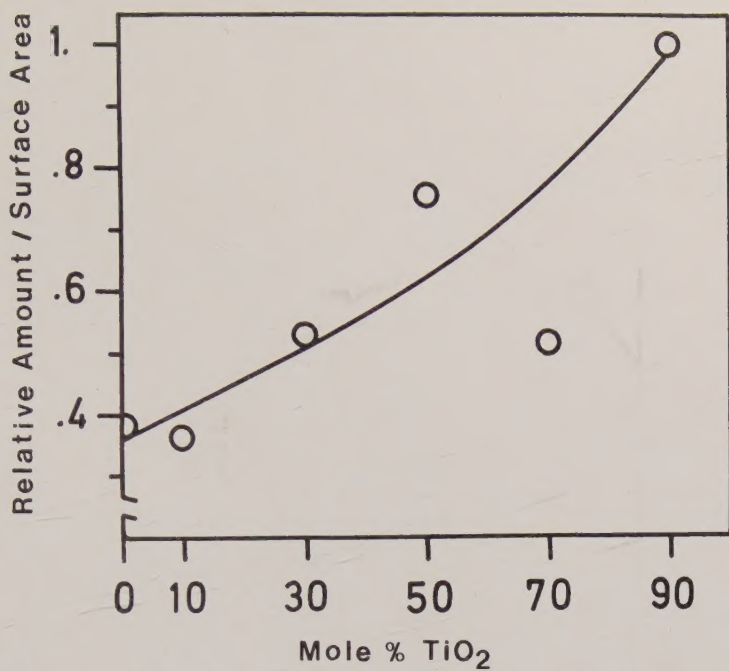


Figure 7. Relative amount per surface area of $(\text{V}=\text{O})_{\text{v}=995}$ as a function of the TiO_2 content.

